QUANTITATIVE DETERMINATION OF TRACE AMOUNTS OF CARBONYL COMPOUNDS. I. THE PREPARATION OF 2-(4'-PHENYLAZO) PHENYLHYDRAZINE SULFONIC ACID

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The compound 2-(4'-phenylazo) phenylhydrazinesulfonic acid or azobezene-*p*-phenylhydrazinesulfonic acid is used in the qualitative trace determination of aldehydes and ketones (Feigl, 1956). The test is carried out in a strongly acidic solution with heating, and the colored reaction product is extracted with chloroform in the presence of ethanol. This reaction has recently been examined in detail and applied to the quantitative determination of trace acetaldehyde in air (Malmberg et al., 1959). The sensitivity and reproducibility of the procedure is greatly dependent upon the reagent quality.

Azobenzene-*p*-phenylhydrazinesulfonic acid is best synthesized by passing sulfur dioxide gas into a benzenediazonium sulfate solution. The original preparation contains several unaccountable features and is vague about the final purification of the product as the ammonium salt (Tröger and Müller, 1908). A latter account mentions the compound as purified via the *p*-toluidine salt (Tröger and Westerkamp, 1909).

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THE OHIO JOURNAL OF SCIENCE 59(6): 322, November, 1959.

Modifications of the old method have now given the acid in better yield. In addition, azobenzene-*p*-phenylhydrazinesulfonic acid has been made by adding sodium phenylhydrazinesulfonate to benzenediazonium sulfate solution. This latter synthesis is new and of interest since it involves a coupling sequence with a negative ion. An alternate route with benzenediazonium chloride solution and benzenediazosulfonate has been stated as not workable (Hodeson and Marsden, 1943). Finally, an attempted bisulfite reduction of diazotized *p*-aminoazobenzene gave only the diazosulfonate here.

EXPERIMENTAL PROCEDURE

Azobenzenephenylhydrazinesulfonic acid. (a) *From aniline.*—Into a three necked 1-l round-bottomed flask equipped with dropping funnel, stirrer, and gas inlet tube and containing 49.0 g (0.50 mole) of concentrated sulfuric acid in 200 ml of water were added with stirring 23.5 g (0.25 mole) of aniline. When the aniline had dissolved, 200 ml of cold water were added and the mixture was chilled to 0° C. A cold solution of 18.0 g (0.26 mole) of sodium nitrate in 35 ml of water was added slowly, so as to maintain the stirred solution below 5° C. The last few milliliters of the nitrate solution were added dropwise, using potassium iodide-starch paper to mark the end point. Sulfur dioxide gas was then bubbled at a rapid rate into the stirred solution over a four-hr period. The clear liquid rapidly changed into a frothy, red suspension which was allowed to stand overnight. The product was collected, washed copiously with cold water, and sucked dry. The reddish-purple material was treated with several portions of boiling benzene to remove soluble impurities, collected and air dried, wt. 19.8 g (55.0%); mp 99.0–100.0°C, with decomposition (block, uncorrected); literature mp 99.0–100.0°C.

Anal. Calcd. for $C_{12}H_{12}N_4O_3S \cdot 1\ 1/4\ H_2O$: C, 45. 78; H, 4. 64; S, 10.19.

Found: C, 45. 94; H, 4. 79; S, 10.04.

For further purification, the acid was dissolved in a hot, saturated ammonium acetate solution and the ammonium salt was allowed to crystallize out. The monohydrate was collected, washed with cold water, and dried: mp 164.0–165.0° C, with decomposition. The free acid was obtained by adding the ammonium azobenzenephenylhydrazinesulfonate monohydrate to cold, dilute mineral acid and collecting the precipitated acid which was washed and dried.

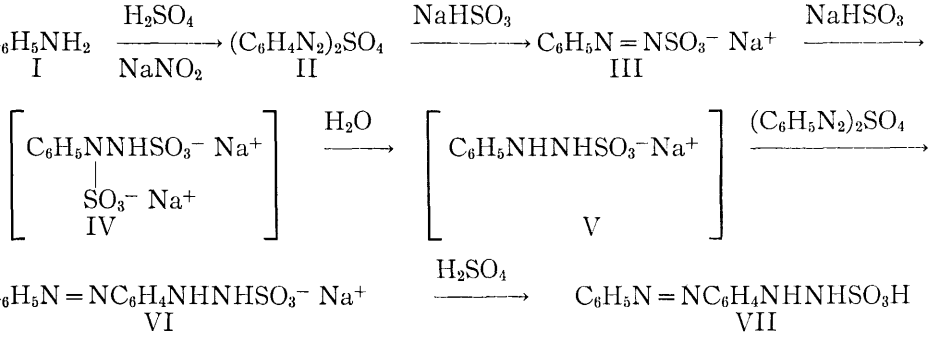
(*b*) *From sodium phenylhydrazinesulfonate.*—As described, 7.75 g (0.082 mole) of aniline were diazotized and 19.0 g (0.082 mole) of sodium phenylhydrazinesulfonate monohydrate (see below) in 100 ml of cold water were added dropwise with stirring. After standing overnight, the solid was collected, washed and dried: wt. 4.4 g (17.0%). In a neutralized diazonium solution, the coupling gave a yield of 6.5 g (25.0%). The infrared spectrum was identical with the material prepared through the use of sulfur dioxide.

(*c*) *From* p-*aminoazobenzene.*—Conventional reduction of diazotized *p*-aminoazobenzene with aqueous sodium bisulfite gave only the insoluble intermediate diazosulfonate. The same result has been reported by other workers (Hodeson and Marsden, 1943).

Sodium phenylhydrazinesulfonate.—The original method was modified as follows (Bücherer and Schmidt, 1909). A mixture of 40 g (0.37 mole) of phenylhydrazine and 400 ml of 36 percent sodium bisulfite solution was refluxed for two days. The solution was extracted with three 200 ml portions of hot benzene and then treated with Darco, filtered, evaporated down to a 100 ml volume, and chilled to give 42.0 g (49.2%) of the monohydrate (three crops): mp 118–120° C (loss of water) and decomposition beginning at 240° C (reported mp 120° C). As a check upon the structure assigned to this compound, 0.1 g was dissolved in 5 ml of water and mixed with 5 ml of commercial Chlorox (sodium hypochlorite solution). An immediate yellow precipitate appeared, due to oxidation of the sodium phenylhydrazinesulfonate to sodium phenylazosulfonate.

DISCUSSION

The mechanism for azobenzene-*p*-phenylhydrazinesulfonic acid formation from aniline may be written as follows:



The intermediates II to V are conventionally written for the conversion of aniline to phenylhydrazine (Rodd, 1954). The sequence V to VI is supported by the observed reaction between sodium phenylhydrazine sulfonate and benzenediazonium sulfate. Also, these coupling reactions are analogous to those between the sodium salt of aniline-ω-methanesulfonic acid and diazonium reagents (Kaplan, 1954).

The infra-red spectrum of azobenzene-*p*-phenylhydrazinesulfonic acid can be rationalized with the accepted structure. The spectrum provides a satisfactory means of evaluating the purity of the reagent. The absorption bands are assigned as follows: 3300 (-NH-), 3030 (Nujol), 3000 (Nujol), 1845 (-C=C-), 1600 (-C=C-), 1585 (-C=C-), 1580 (-N=N-), 1475 (Nujol), 1380 (Nujol), 1340 (-C-N), 1338 ($-SO_2-$), 1240 ($-NHSO_3H$), 1150 ($-SO_2-$), 1083 (mono or 1,4 substitution), 1050 ($-SO_3H$), 1000 (mono or 1,4 substitution), 840 (1,4 substitution), 825 (phenyl), 760 (Nujol), and 755 (monosubstitution) cm^{-1}.

ACKNOWLEDGMENT

This research was supported by the United States Air Force under Contract AF 33(600)-30287, monitored by the Aero Medical Laboratory of the Air Research and Development Command, Lt. Lawrence F. Eng, Project Engineer.

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